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Propyltrimethoxysilane-thiolate Iron and Nickel Complexes: Synthesis, Characterization and Electrochemical Behaviour

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Abstract

The new thiolate-bridged nickel dimer $[Ni(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3(OMe)_3\}]_2$ (**1**), has been obtained by reaction of 3-mercaptopropyltrimethoxysilane with nickelocene. Thermal reaction between $[Fe(CO)_2(\eta\text{-}C_5H_5)]_2$ and the disulphide $[S(CH_2)_3Si(OMe)_3]_2$ in cyclohexane gives the dinuclear thiolate-bridged complex $[Fe(CO)(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2$ (**2**), which can be isolated as two isomeric forms. Oxidation of **2** can be achieved by treatment with ferricinium hexafluorophosphate, resulting in the paramagnetic monocationic dinuclear species $[Fe(CO)(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2PF_6$ (**3**). Reaction of $[Fe(CO)_2(\eta\text{-}C_5R_5)Br]$ (R = H or Me) with $HS(CH_2)_3Si(OMe)_3$ in the presence of Et_3N, or with $NaS(CH_2)_3Si(OMe)_3$, in THF solution affords the mononuclear thiolate derivatives $[Fe(CO)_2(\eta\ C_5R_5)\{S(CH_2)_3Si(OMe)_3\}]$ (R = H (**4**) or Me (**5**)). The electrochemical behaviour of the synthesized complexes has been studied using cyclic voltammetry and coulometry. The dinuclear species **1** and **2** have been oxidized voltammetrically and monocationic $\mathbf{1}^+$ and $\mathbf{2}^+$ and dicationic $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ species have been detected, $\mathbf{1}^+$ and $\mathbf{2}^+$ being characterized by ESR spectroscopy. The electrochemical oxidation of the mononuclear complexes **4** and **5** is followed by the elimination of $^{\bullet}[S(CH_2)_3Si(OMe)_3]$, the cationic species $[Fe(CO)_2(\eta\text{-}C_5R_5)(THF)]^+$ or $[Fe(CO)_2(\eta\text{-}C_5H_5)(PPh_3)]^+$ being detected if the oxidation is carried out in the presence of PPh_3.

Introduction

In recent years we have been interested in the synthesis and study of new organometallic complexes that contain alkoxysilane and siloxane ligands [1–3]. This choice was made in order to compare the properties and reactivity of these monomers with those of the corresponding polymers we intend to prepare in the near future.

We have recently reported the synthesis of some iron complexes that contain alkoxysilane functionalized cyclopentadienyl ligands [1]. As a continuation of these studies we have now prepared new iron and nickel complexes in which the alkoxysilane group is directly bonded to the metal atom. Both types of compounds can be attached to the metal oxides surfaces and used in catalytic reactions (supported catalysis) [4]. Moreover, they can be attached to the metallic electrode surface, modifying its properties, in order to study the application of the electrodes, modified in this way, in electrocatalytic processes [5, 6].

We report here full details of the synthesis and characterization of new binuclear iron and nickel complexes $[Ni(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2$ (**1**), $[Fe(CO)(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2$ (**2**) and its monocationic derivative $[Fe(CO)(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2PF_6$ (**3**), which contain propyltrimethoxysilane-thiolate bridges; and also the mononuclear iron complexes $[Fe(CO)_2(\eta\text{-}C_5R_5)\text{-}\{S(CH_2)_3Si(OMe)_3\}]$ (R = H (**4**) and Me (**5**)). In addition the electrochemical behaviour of the complexes is reported and discussed.

Experimental

All reactions and manipulations were carried out under oxygen-free nitrogen using Schlenk techniques. Tetrahydrofuran (THF) and diethylether were distilled from sodium benzophenone-ketyl under nitrogen just before use. Dichloromethane, n-hexane and cyclohexane were distilled from phosphorus pentoxide. Acetonitrile was refluxed over P_2O_5 and distilled, then refluxed over calcium hydride and distilled under nitrogen. Infrared spectra were

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recorded in the range 4000–200 cm^{-1} on a Nicolet 5DX-FT-IR spectrophotometer using CsI windows. The solution spectra were examined in a 0.1 mm cell with KBr windows. The ^1H NMR spectra were recorded on a Bruker WH-200-5Y (200 MHz, Fourier Transform mode) spectrometer. Chemical shifts (δ) are reported in ppm with reference to internal $SiMe_4$. The EPR spectra were recorded on a Varian E-12 spectrometer at a microwave frequency of 9 GHz (X-band) equipped with a HP5342A frequency-meter and a Bruker NMR gaussmeter.

Bis(propyltrimethoxysilane)disulphide, $S_2[(CH_2)_3$-$Si(OMe)_3]_2$ was prepared by oxidation of 3-mercaptopropyltrimethoxysilane with iodine, in the presence of pyridine in CCl_4 solution, and purified by distillation *in vacuo* (60 °C, 10 mm). Alternatively, this disulphide can be obtained by oxidation of the thiol $HS(CH_2)_3Si(OMe)_3$ with SO_2Cl_2 according to the literature procedure [7]. The compounds $[Fe(CO)_2(\eta$-$C_5R_5)]_2$, $[Fe(CO)_2(\eta$-$C_5R_5)Br]$ (R = H or Me) and $[Ni(\eta$-$C_5H_5)_2]$ were synthesized by the literature procedures [8–12].

For the purification of the compounds via column chromatography, silica pretreated with Me_3SiCl according to the literature procedure [13] was used. Commercial silanized silica (Merck) can also be used.

The electrochemical apparatus, techniques and measurements have been described previously [14]. In the coulometry study a PAR Model 377A coulometry cell system was used.

In situ ESR measurements of the cations 1^+ and 2^+ derived electrooxidatively were carried out in a three-electrode spectroelectrochemical home-made cell (Fig. 1).

Synthesis of Complexes

$[Ni(\eta$-$C_5H_5)\{\mu$-$S(CH_2)_3Si(OMe)_3\}]_2$ (1)

To a degassed and stirred benzene solution (40 cm^3) of $[Ni(\eta$-$C_5H_5)]_2$ (1.5 g, 7.94 mmol), 3-mercaptopropyltrimethoxysilane (3.1 g, 15.80 mmol) in 10 cm^3 of C_6H_6 was added dropwise, at room temperature. Immediate reaction is indicated by a colour change from green to dark brown. The stirred mixture was kept at 25 °C for 15 h. After removal of the solvent, the residue was dissolved in n-hexane/THF mixture (3:1), and the brown solution placed on a chromatography column (silanized silica, 3 × 30 cm). Elution with n-hexane gave a single brown band. The solvent was removed *in vacuo* to give the product finally isolated as a brown oil. Yield 85%. *Anal.* Calc. for $C_{22}H_{40}Ni_2O_6S_2Si_2$: C, 41.4; H, 6.8; Ni, 18.5. Found: C, 41.9; H, 6.1; Ni, 18.2%. δ H($CDCl_3$) 0.72 (2H, t, CH_2-Si); 1.80 (2H, m, CH_2); 2.50 (2H, t, CH_2-S); 3.55 (9H, s, $(OCH_3)_3$); 5.25 (5H, s, C_5H_5).

cis-$[Fe(CO)(\eta$-$C_5H_5)\{S(CH_2)_3Si(OMe)_3\}]_2$ (cis-2)

A solution of $[Fe(CO)_2(\eta$-$C_5H_5)]_2$ (1.5 g, 4.23 mmol) and $[S(CH_2)_3Si(OMe)_3]_2$ (2.6 g, 6.72 mmol) in cyclohexane (50 cm^3) was heated at 75–80 °C for 12 h. The formation of 2 was monitored by IR spectroscopy (the initial ν(CO) bands of $[Fe(CO)_2(\eta$-$C_5H_5)]_2$ at 2004, 1960 and 1796 cm^{-1}, give way to new bands at 1954vs and 1923w). Elimination of the solvent *in vacuo* gives a brown residue which is dissolved in a minimum of cyclohexane/n-hexane (2/1) mixture and transferred to a column chromatography with silanized silica. Elution with cyclohexane/n-hexane mixture solvents afforded a strong single brown band which was collected. The solvent was removed, and complex *cis*-2 was finally isolated as a brown oil, yield 80%. *Anal.* Calc. for $C_{24}H_{40}Fe_2$-$O_8S_2Si_2$: C, 41.8; H, 5.8; Fe, 16.3. Found: C, 41.6; H, 5.1; Fe, 16.9%. δ H(($CDCl_3$) 0.75 (2H, t, CH_2-Si); 1.90 (2H, m, CH_2); 2.73 (2H, t, CH_2-S); 3.57 (9H, s, $(OCH_3)_3$); 4.46 (5H, s, C_5H_5).

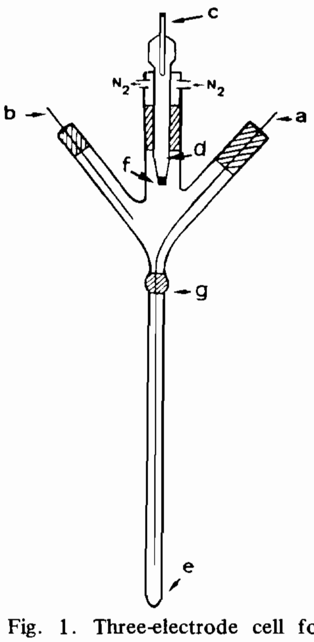


Fig. 1. Three-electrode cell for controlled-potential electrolysis as followed by ESR spectroscopy: (a) working electrode (platinum wire); (b) auxiliary electrode; (c) reference electrode (SCE); (d) salt bridge of $[NBu^n{}_4][PF_6]$ in non-aqueous solvent; (e) quartz tube; (f) Vycor fritt; (g) Teflon joint.

trans-$[Fe(CO)(\eta$-$C_5H_5)\{\mu$-$S(CH_2)_3Si(OMe)_3\}]_2$ (trans-2)

A solution of *cis*-2 (ν(CO) 1954vs, 1923w) in cyclohexane at 10 °C was irradiated with ultraviolet light until conversion to the *trans*-2 isomer ceased, as determined by monitoring the reaction by IR spectroscopy (*trans*-2 ν(CO) 1944m, 1930s). The solvent was removed *in vacuo* and the residue purified chromatographically on silanized silica, using cyclohexane–petroleum ether (1:3) mixture as eluent. The conversion of *cis*-2 into *trans*-2 was about 85–90%. δ H($CDCl_3$) 0.80 (2H, m, CH_2-Si); 1.98 (2H, m, br, CH_2); 2.97 (2H, m, br, CH_2-S); 3.75 (9H, m, $(OCH_3)_3$); 4.45 (5H, s, C_5H_5).

$[Fe(CO)(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2PF_6$ (3)

To a CH_2Cl_2 solution (30 cm^3) of *cis*-2 (1.7 g, 2.54 mmol), $[Fe(\eta\text{-}C_5H_5)_2]PF_6$ (0.4 g, 1.25 mmol) was added at room temperature. The mixture was stirred for 5 h, a colour change from brown to green being observed. The total conversion of the neutral dimer (ν(CO) band at 1943s cm^{-1}) into the monocationic complex 3 (ν(CO) at 2008s, 1986w) was confirmed by IR spectroscopy. After concentration to 5 cm^3, addition of diethyl ether (60 cm^3), and filtration, the complex was isolated as an air-stable green crystalline solid, which was recrystallized in CH_2Cl_2/diethyl ether (1:2). Yield 90%. *Anal.* Calc. for $C_{24}H_{40}Fe_2O_8Si_2S_2F_6P$: C, 34.6; H, 4.9; Fe, 13.4%. Found: C, 34.4; H, 4.7; Fe, 13.8%.

$[Fe(CO)_2(\eta\text{-}C_5R_5)\{S(CH_2)_3Si(OMe)_3\}]$

Method (a). R = Me (5). To a stirred THF suspension of sodium hydride (0.3 g, 12.5 mmol) (30 cm^3 of THF), mercaptopropyltrimethoxysilane (3.5 g, 17.6 mmol) was added dropwise at room temperature. The mixture was stirred until effervescence ceased (1 h). $[Fe(CO)_2(\eta\text{-}C_5Me_5)Br]$ (3.9 g, 12.0 mmol) in 10 cm^3 of THF was added dropwise and the mixture was stirred for 15 h at room temperature. After filtration of the NaBr, the solvent was removed *in vacuo* and the residue was column chromatographied on silanized silica using THF/n-hexane (1:2) for elution. The single red–brown band was collected and the solvent removed *in vacuo* to give 5 as a dark red oil. *Anal.* Calc. for $C_{18}H_{23}FeO_5SSi$: C, 49.6; H, 5.2; Fe, 12.8. Found: C, 49.9; H, 5.1; Fe, 12.6%. δ H($CDCl_3$) 0.68 (2H, t, CH_2-Si); 1.75 (2H, m, CH_2); 1.90 (15H, s, $(CH_3)_3$); 2.95 (2H, m, CH_2-S); 3.70 (9H, s, $(OCH_3)_3$).

R = H (4). Following the procedure described above, complex 4 was prepared from $[Fe(CO)_2(\eta\text{-}C_5H_5)Br]$ (1.5 g, 5.83 mmol) and $NaS(CH_2)_3Si(OMe)_3$ (1.7 g, 7.78 mmol). *Anal.* Calc. for $C_{13}H_{20}O_5FeSSi$: C, 41.9; H, 5.4; Fe, 15.0. Found: C, 41; H, 5.1; Fe, 15.2%. δ H($CDCl_3$) 0.67 (2H, t, CH_2-Si), 1.75 (2H, m, CH_2); 2.65 (2H, t, CH_2-S); 3.53 (9H, s, $(OCH_3)_3$); 4.98 (5H, s, C_5H_5).

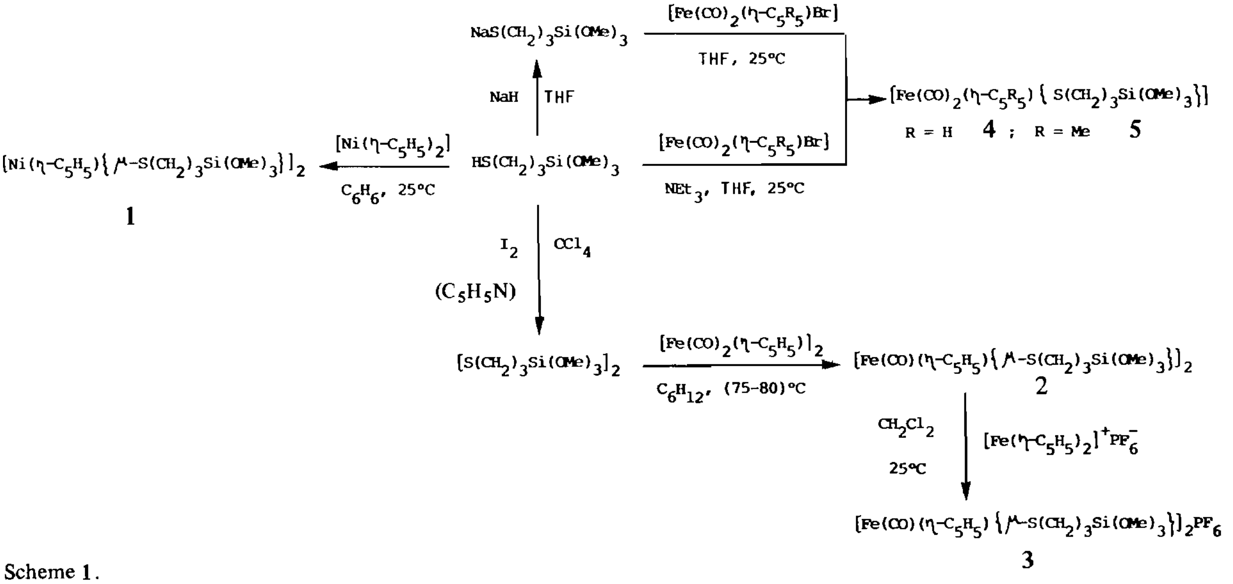
Method (b). R = H (4). To a degassed and stirred THF solution (30 cm^3) of $[Fe(CO)_2(\eta\text{-}C_5H_5)Br]$ (1 g, 3.9 mmol), the thiol $HS(CH_2)_3Si(OMe)_3$ (1.2 g, 6.0 mmol) was added, and then triethylamine (0.65 g, 6.5 mmol) was added dropwise. The mixture was stirred for 20 h at room temperature. After filtration of the $HNEt_3Br$ and concentration, the complex was isolated following the same procedure described in method (a).

R = Me (5). A similar procedure was used with $[Fe(CO)_2(\eta\text{-}C_5Me_5)Br]$ (1 g, 3.0 mmol), $HS(CH_2)_3Si(OMe)_3$ (1 g, 5.0 mmol) and Et_3N (0.55 g, 5.5 mmol). Complex 5 was isolated as a dark red oil as described previously.

Results and Discussion

Synthesis of the Binuclear Complexes

Nickelocene reacts readily with 3-mercaptopropyltrimethoxysilane to give the dinuclear complex $[Ni(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2$ (1) (Scheme 1). This reaction takes place smoothly and quantitatively



Scheme 1.

in benzene or n-hexane as solvents, at room temperature, to give a brown compound. Its purification can be accomplished by column chromatography provided the silica is previously silanized. If normal silica or neutral alumina is used, the compound remains on the column, due to the attachment of the hydrolyzable $Si(OMe)_3$ groups to the silica or alumina surfaces.

In the pure form complex **1** exists as a dark brown oil at room temperature. Attempts to crystallize this compound were unsuccessful, due to its extremely high solubility in solvents such as n-hexane or n-pentane, even at low temperatures (*c.* −70 °C). The determination of the molecular weight and the diamagnetism of **1** confirms a dinuclear structure in which the dimerization is believed to occur via thiolate bridges. Evidence of a π-bonded cyclopentadienyl ring and the presence of $S(CH_2)_3Si(OMe)_3$ was obtained from the IR and ^1H NMR spectra.

Treatment of $[Fe(CO)_2(\eta\text{-}C_5H_5)]_2$ with the disulphide $S_2[(CH_2)_3Si(OMe)_3]_2$ in cyclohexane at 75 °C leads to the formation of the dinuclear derivative $[Fe(CO)(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2$ (**2**) (Scheme 1). It is relevant to note that monitoring the reaction by IR spectroscopy revealed that after 3 h new medium bands at 2024 and 1975 cm^{-1} appear, which correspond to the formation of the intermediate mononuclear dicarbonyl species $[Fe(CO)_2(\eta\text{-}C_5H_5)\{S(CH_2)_3Si(OMe)_3\}]$ (**4**) (see later and Table 1), which dimerizes by thermal treatment, it then being observed that these bands disappear and give place to a new strong band at 1954 cm^{-1} corresponding to the formation of the binuclear complex **2**. The dinuclear nature of this complex was confirmed by determination of its molecular weight.

We also attempted to synthesize the pentamethylcyclopentadienyl binuclear analogous complex by reaction of the bis(propyltrimethoxysilane) disulphide with $[Fe(CO)_2(\eta\text{-}C_5Me_5)]_2$ but the behaviour of this iron dimer is significantly different. Thus, under the same conditions (cyclohexane, 75 °C), the reaction affords a mixture of mononuclear $[Fe(CO)_2(\eta\text{-}C_5Me_5)\{S(CH_2)_3Si(OMe)_3\}]$ (**5**) and the binuclear thiolate–pentamethylcyclopentadienyl complex $[Fe(CO)(\eta\text{-}C_5Me_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2$. The formation of this binuclear compound is probably difficult because of stereoelectronic reasons due to the pentamethylcyclopentadienyl ligand. The steric hindrance arising from the greater size of the $\eta\text{-}C_5Me_5$ ring, (the cone angle for $\eta\text{-}C_5H_5$ is 110° whereas for the $\eta\text{-}C_5Me_5$ ring it is 142° [15]) in part prevents the dimerization of the mononuclear species **5**. In addition owing to the presence of the $\eta\text{-}C_5Me_5$ ring the metal centre in **5** is more basic than that in **4**, as is confirmed by the electrochemical results, and therefore **5** is less susceptible to a nucleophilic attack by the sulphur atom than compound **4**. All our attempts to separate (by column chromatography or by crystallization in various solvents) the mono and binuclear pentamethylcyclopentadienyl complexes were unsuccessful.

It has previously been reported that most compounds $[Fe(CO)(\eta\text{-}C_5H_5)(\mu\text{-}SR)]_2$ occur in two isomeric forms which differ in stability and spectral properties: an 'A' isomer, which is stable at ambient and elevated temperatures, and a 'B' isomer, which is unstable with respect to 'A' under these conditions [16]. The strong ν(CO) stretching frequency of isomer 'A' is about 20 to 40 cm^{-1} higher than that of isomer 'B' [17, 18].

We have found that thermal treatment (75 °C, in C_6H_{12}) of $[Fe(CO)_2(\eta\text{-}C_5H_5)]_2$ and the disulphide $[S(CH_2)_3Si(OMe)_3]_2$, leads only to the formation of the binuclear compound **2** whose ^1H NMR spectrum shows single and sharp cyclopentadienyl signals, and a single resonance for each group of the propyltrimethoxysilane substituent. In addition, the IR spectrum in cyclohexane solution exhibits a strong

TABLE 1. Characteristic and comparative IR ν(CO) data (cm^{-1}) for the iron complexes

Complex	ν(CO) [a]
$[Fe(CO)_2(\eta\text{-}C_5H_5)\{S(CH_2)_3Si(OMe)_3\}]$ [b] (**4**)	2024s, 1975s
$[Fe(CO)_2(\eta\text{-}C_5Me_5)\{S(CH_2)_3Si(OMe)_3\}]$ [b] (**5**)	2006s, 1958s
cis-$[Fe(CO)(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2$ (**2**)	1954s, 1923w
trans-$[Fe(CO)(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2$ (**2**)	1944m, 1930s
$[Fe(CO)(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2PF_6$ (**3**)	2008s, 1986w [c]
cis-$[Fe(CO)(\eta\text{-}C_5H_5)\{\mu\text{-}SMe\}]_2$ [d]	1957s, 1926w
trans-$[Fe(CO)(\eta\text{-}C_5H_5)\{\mu\text{-}SMe\}]_2$ [d]	1946m, 1936s
cis-$[Fe(CO)(\eta\text{-}C_5H_5)\{\mu\text{-}SEt\}]_2$ [d]	1955s, 1926w
trans-$[Fe(CO)(\eta\text{-}C_5H_5)\{\mu\text{-}SEt\}]_2$ [d]	1944m, 1931s
cis-$[Fe(CO)(\eta\text{-}C_5H_5)\{\mu\text{-}S^iPr\}]_2$ [d]	1953s, 1925w
trans-$[Fe(CO)(\eta\text{-}C_5H_5)\{\mu\text{-}S^iPr\}]_2$ [d]	1946m, 1931s

[a] In cyclohexane. [b] Force constant in mdyn $Å^{-1}$: 16.24 for 4 and 15.85 for 5. [c] Data in CH_2Cl_2. [d] Values taken from refs. 17 and 19.

ν(CO) band at 1954 cm^{-1} and a weak band at 1923 cm^{-1}. These data agree with those reported for several *cis*-[Fe(CO)(η-C_5H_5){μ-SR}]$_2$ isomers as can be seen in Table 1.

However, if a mixture of bis(cyclopentadienyl iron dicarbonyl) and the disulphide of bis(propyltrimethoxysilane) was irradiated with UV light, at 20 °C, a different isomer of 2, 'B', was obtained, whose NMR spectrum exhibits broadening in the resonance of the (CH_2)Si(OMe)$_3$ groups, and whose IR spectrum, in C_6H_{12} solution, gives a ν(CO) strong band at lower frequency (1930s, 1944m, cm^{-1}, Table 1).

By analogy with previous studies, it is now suggested that, the first isomer described, isomer stable 'A' of 2 with a higher strong ν(CO) band, contains the two cyclopentadienyl groups *cis*-disposed with respect to the Fe_2S_2 ring, while, isomer 'B' contains them *trans*-disposed.

In addition, UV photolysis of a C_6H_{12} solution at 20 °C of isomer 'A' causes isomerization to compound 'B'. Heating of solutions of isomer 'B' readily converted it to isomer 'A'. These results contrast with previously reported results in which in some complexes [Fe(CO)(η-C_5H_5)(μ-SR)]$_2$ (R = t-C_4H_9, CH_2-(C_6H_5)), all attempts to convert the isomer 'A' into isomer 'B' have proved unsuccessful [17].

On the other hand, see 'Electrochemical Studies', the relatively low value of the anodic potential of the first reversible oxidation of complex 2, reveals that probably this compound can be oxidized by mild chemical reagents. Thus, we found that ferricinium hexafluorophosphate [(η-C_5H_5)$_2$Fe]PF_6, is a very efficient and clean reagent for effecting the oxidation of the neutral dimer. 2 (as isomer stable 'A'), to give the monocationic paramagnetic species [Fe(CO)(η-C_5H_5){μ-S(CH_2)$_3$Si(OMe)$_3$}]$_2PF_6$ (3). In practice, this oxidation proceeds readily at room temperature, in CH_2Cl_2 solution, a colour change from brown to green being observed, as well as the corresponding change in the IR spectrum. After precipitation with ether the complex was isolated as an air-stable green crystalline solid. The solution IR spectrum of this monocation shows essentially a single peak in the ν(CO) region (2008s, 1986vw cm^{-1}) (Table 1), which suggests that this species corresponds to the *cis*-isomer, in agreement with the IR ν(CO) values reported for the *cis*-isomer of [Fe(CO)(η-C_5H_5)(μ-SR)]$_2$X (X = I_3, PF_6, SbF_6, BPh_4) [19, 20].

The ESR spectrum of 3 in CH_2Cl_2 solution at room temperature exhibits an isotropic value of $\langle g \rangle$ = 1.995 ($S = 1/2$), which is very similar to the spin-only value. The anisotropic g values obtained by taking measurements in frozen CH_2Cl_2 solution (at N_2 liquid temperature) are $g_1 = 2.033$, $g_2 = 2.013$ and $g_3 = 1.939$, data which are in agreement with the ESR values reported for cationic complexes of the type [Fe(CO)(η-C_5H_5)μ-SR]$_2^+$ [20, 21].

Synthesis of the Mononuclear Iron Complexes

We are also interested in the preparation of mononuclear complexes with the thiolate –S(CH_2)$_3$Si(OMe)$_3$ terminal ligand. A possible method for the synthesis of this type of complex is the nucleophilic displacement of halogens by mercaptide anions [22] under non-hydroxylic conditions. In this way, the sodium salt of 3-mercaptopropyltrimethoxysilane, obtained by slow addition of the thiol to NaH in THF solution, reacted readily with both cyclopentadienyl derivatives [Fe(CO)$_2$(η-C_5R_5)Br] (R = H or Me), as shown in Scheme 1.

The only products of this reaction are the mononuclear thiolate complexes **4** and **5**. The new complexes are formed in *c.* 85% isolated yield, and after the purification by column chromatography on silica previously silanized, were obtained as red or brown oils.

Another method that also leads to the formation of complexes **4** and **5** is the direct reaction of the thiol HS(CH_2)$_3$Si(OMe)$_3$ with [Fe(CO)$_2$(η-C_5R_5)Br] (R = H, Me) in the presence of triethylamine, in THF solution, as depicted in Scheme 1.

The IR spectra of these complexes display strong absorption characteristic of the –S(CH_2)$_3$Si(OMe)$_3$ ligand in the 1200–1000 cm^{-1} and 810 cm^{-1} regions, due to ν_s and ν_{as}(SiOC) vibrations. In the ν(CO) region (see Table 1), the compounds show the expected two strong carbonyl bands for complexes of the type Fe(CO)$_2$(η-C_5R_5)L. These ν(CO) values and also the corresponding force constants, show an important decrease on going from complex **4** with a η-C_5H_5 ring to the parent complex **5** with η-C_5Me_5 as a consequence of the higher electron donor ability of the pentamethylcyclopentadienyl ligand.

Electrochemical Studies

Binuclear complexes

An ambient temperature cyclic voltammogram of the binuclear thiolate-bridged nickel complex (1) in 0.1 mol dm^{-3} [NBu^n_4] [PF_6] acetonitrile solutions at a carbon glassy electrode is shown in Fig. 2. The electrochemical parameters are listed in Table 2. Cyclic voltammetry (CV) shows two anodic (A and B) and a cathodic (A′) peaks. Potentiostatic coulometry and comparisons of the limiting currents obtained from rotating disk electrode RDE voltammograms between the nickel complex 1 with [Fe(CO)$_2$(η-C_5H_5)]$_2$ indicate two successive one-electron transfers. These electrochemical processes are diffusion controlled with the anodic current function ($i_{p_a}/\nu^{1/2}$) independent of scan rate (ν) over the range 0.1–1 V s^{-1}. The CV curves reveal that the first electron transfer can be associated with a reversible process, the peak separation ΔE_p(A/A′) being 60 mV at 0.2 V s^{-1}. The peak current ratio, $i_{p_c}/i_{p_a} \approx 1$ (i_{p_c} = cathodic return peak current, i_{p_a} = anodic peak

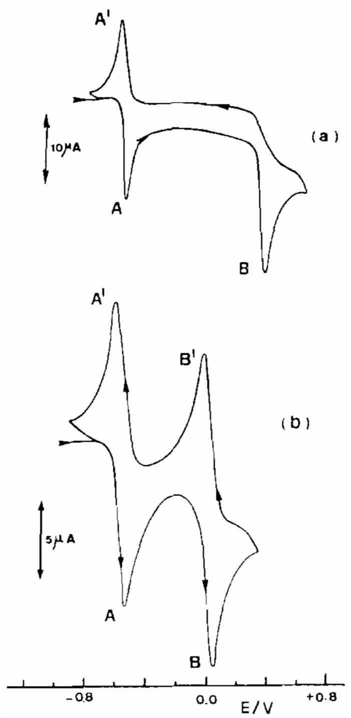


Fig. 2. Cyclic voltammograms in CH_3CN solution at a carbon glassy electrode for: (a) $[\mathrm{Ni}(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2$ (1), scan rate 0.2 V s^{-1}; (b) $[\mathrm{Fe(CO)}(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_2\}]_2$ (*cis*-2), scan rate 0.2 V s^{-1}.

current), indicates that a chemically reversible process takes place, and a stable monocationic species, in the CV time scale, is originated. The existence of this monocationic species has been proved by controlled potential electrolysis in the ESR cavity. The paramagnetic species formed in the first oxidation step (at potentials 100 mV more positive than E_pA) show at room temperature a single ESR signal, $\langle g \rangle = 2.040$. At lower temperatures (N_2 liquid) an anisotropic spectrum with two g values ($g_1 = 2.084$; $g_2 = 1.995$) was found. These results were in agreement with those previously reported [21] for other paramagnetic species of the type $[\mathrm{Ni}(\eta\text{-}C_5H_5)(\mu\text{-}SR)]_2^+$.

Although chemical or electrochemical oxidation of complex **1** clearly affords the monocation **1**$^+$, attempts to isolate this species were unsuccessful. The results for nickel complex **1** can be summarized as follows:

$$[\mathrm{Ni}(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2$$

$$+e^- \; A' \;\; \uparrow\downarrow \;\; A - e^-$$

$$[\mathrm{Ni}(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2^+$$

$$\downarrow \;\; B - e^-$$

$$[\mathrm{Ni}(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2^{2+}$$

The cyclic voltammogram of the binuclear iron complex 2 (*cis*-isomer), in acetonitrile solution at a carbon glassy electrode, displays two anodic peaks (A and B) and the corresponding cathodic peaks (A' and B') (Fig. 2 and Table 2). Potentiostatic coulometry and comparisons of the limiting currents obtained from the RDE voltammograms between complex 2 with $[\mathrm{Fe(CO)}_2(\eta\text{-}C_5H_5)]_2$ indicate two one-electron transfers. Both systems A/A' and B/B' are diffusion controlled and correspond to reversible electrochemical processes, ΔE_p being about 60 mV and $i_{p_c}/i_{p_a} \approx 1$ over the scan range studied. The electrochemical data can be rationalized in terms of the following scheme:

$$[\mathrm{Fe(CO)}(\eta\text{-}C_5H_5)\}\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2$$

$$+3^- \; A' \;\; \uparrow\downarrow \;\; A - e^-$$

$$[\mathrm{Fe(CO)}(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2^+$$

$$+e^- \; B' \;\; \uparrow\downarrow \;\; B - e^-$$

$$[\mathrm{Fe(CO)}(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2^{2+}$$

The formation of the monocationic species 2^+ is confirmed by *in situ* ESR spectroelectrochemistry. The species found in the first oxidation step is paramagnetic and exhibits a simple broad ESR signal ($\langle g \rangle = 1.995$) at room temperature. In liquid nitrogen, the ESR spectrum is anisotropic, Fig. 3, and the three values of the g tensor are coincident with the values obtained for the chemically prepared monocationic

TABLE 2. Cyclic voltammetric[a] data for the complexes at 200 mV s^{-1}

Compound	E_A	$E_{A'}$	ΔE_p (mV)	E_B	$E_{B'}$	ΔE_p (mV)	E_I	E_{II}	$E_{II'}$
1[b]	−0.52	−0.58	60	+0.42					
2[b, c]	−0.55	−0.62	70	+0.05	−0.01	60			
4[d]							+0.79	−0.05	−1.73
5[d]							+0.25	−1.4	−1.91

[a] At a carbon glassy electrode. Potentials quoted vs. $[\mathrm{Fe}(\eta\text{-}C_5H_5)_2]^+$–$[\mathrm{Fe}(\eta\text{-}C_5H_5)_2]$ couple. [b] Solvent: CH_3CN. [c] *cis*-isomer.
[d] Solvent: THF.

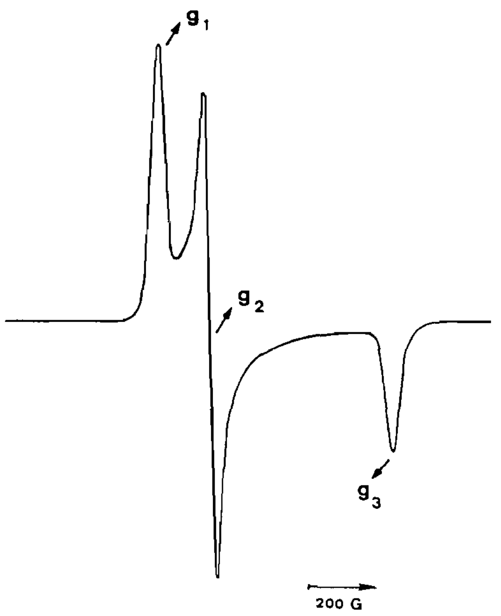


Fig. 3. ESR spectrum of the electrochemically generated monocationic complex $[Fe(CO)(\eta\text{-}C_5H_5)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}]_2PF_6$, in frozen CH_3CN solution, at N_2 liquid temperature.

complex 3. In addition, the CV curves of 3 in acetonitrile solutions resulting from electrochemical oxidation or reduction indicate reversible systems. The cathodic and anodic potential peaks of these couples of 3 are identical with those peak potentials of the systems (B/B′) and (A/A′) of the neutral dimer 2 respectively.

Mononuclear iron complexes

The oxidative electrochemistry of the synthesized compounds 4 and 5 was investigated in THF with $[NBu^n_4][PF_6]$ as supporting electrolyte. Electrochemical parameters for the complexes are summarized in Table 2.

The cyclic voltammograms show anodic (I) and cathodic (II) peaks, but they are not associated with a reversible oxidation–reduction process, because of a large peak separation and a i_{p_c}/i_{p_a} value much smaller than unity (Table 2). The irreversibility of the process corresponding to peaks I and II was confirmed by the magnitude of the slopes in the plots of E_p versus $\log \nu$ which are significantly larger than those expected for a reversible process. These anodic oxidations are irreversible at scan rates as high as $5\ V\ s^{-1}$.

Bulk oxidation of complexes 4 and 5, carried out at a potential 100 mV more positive than the anodic potentials results in the removal of 1.0 electron per molecule.

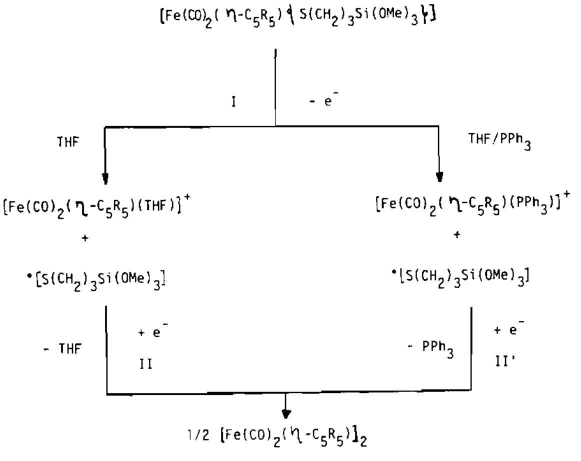
The anodic and cathodic peaks for complex 5 shift to more cathodic potentials in accordance with the greater donor ability of the $\eta\text{-}C_5Me_5$ ligand.

Addition of PPh_3 to the solutions of complexes 4 and 5 significantly modifies the CV curves obtained. It is observed that the reduction peaks II disappear and new reduction peaks (II′) appear at less positive potentials (see Table 2). These cathodic peak potentials are identical with the reduction peak potential observed in the CV of the THF solutions of $[Fe(CO)_2(\eta\text{-}C_5H_5)(PPh_3)]^+$ and $[Fe(CO)_2(\eta\text{-}C_5Me_5)(PPh_3)]^+$ respectively, previously chemically obtained; this fact confirms the elimination of $\cdot[S(CH_2)_3Si(OMe)_3]$ after oxidation.

On the other hand, it is known that the electrochemical oxidation of the dimer $[Fe(CO)_2(\eta\text{-}C_5H_5)]_2$ gives cationic species of the type $[Fe(CO)_2(\eta\text{-}C_5H_5)S]^+$ (S = solvent) [23, 24]. When this process is carried out in the presence of added nucleophiles, such as PPh_3, cations such as $[Fe(CO)_2(\eta\text{-}C_5H_5)(PPh_3)]^+$ are formed. The electroreduction of these cations affords the original dimer [1, 25].

The CV of $[Fe(CO)_2(\eta\text{-}C_5H_5)]_2$ in pure THF solutions and with the presence of PPh_3, exhibit cathodic peaks corresponding, respectively, to the reduction of $[Fe(CO)_2(\eta\text{-}C_5H_5)(THF)]^+$ and $[Fe(CO)_2(\eta\text{-}C_5H_5)(PPh_3)]^+$ formed in the anodic sweep. These cathodic peaks voltages are identical to the potentials of peaks II and II′, respectively.

The experimental results are consistent with the following:



R = H, Me
THF = tetrahydrofuran

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